

AD A013360



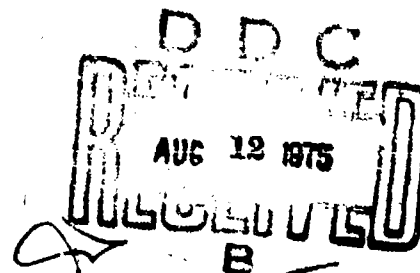
FG
12

COPY NO. 35

TECHNICAL REPORT 4704

**SUBSTITUTION OF ALUMINUM FOR MAGNESIUM
AS A FUEL IN FLARES**

B. JACKSON, JR.
F. R. TAYLOR
R. MOTTO
S. M. KAYE



JANUARY 1975

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED.

**PICATINNY ARSENAL
DOVER, NEW JERSEY**

The findings in this report are not to be construed
as an official Department of the Army Position.

DISPOSITION

Destroy this report when no longer needed. Do not
return it to the originator.

ACCESSION for	
NTIS	White Section <input checked="" type="checkbox"/>
DOC	Buff Section <input type="checkbox"/>
UNANNOUNCED	<input type="checkbox"/>
JUSTIFICATION.....	
BY.....	
DISTRIBUTION/AVAILABILITY CODES	
Dial.	AVAIL. AND/OR SPECIAL
A	

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
⑨ Technical Report 4704	⑭	PA-TR-4704
4. TITLE (and Subtitle)		5. TYPE OF REPORT & PERIOD COVERED
⑥ SUBSTITUTION OF ALUMINUM FOR MAGNESIUM AS A FUEL IN FLARES.		
7. AUTHOR(s)		8. CONTRACT OR GRANT NUMBER(s)
⑩ B. Jackson, Jr., F.R./Taylor, R./Motto S. M./Kaye		⑫ 44 p.
9. PERFORMING ORGANIZATION NAME AND ADDRESS		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
Feltman Research Laboratory Picatinny Arsenal, Dover, NJ		AMCMS 4110.16.4132.7
11. CONTROLLING OFFICE NAME AND ADDRESS		12. REPORT DATE
		⑪ January 1975
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		13. NUMBER OF PAGES
		46
		15. SECURITY CLASS. (of this report)
		Unclassified
		16a. DECLASSIFICATION/DOWNGRADING SCHEDULE
18. DISTRIBUTION STATEMENT (of this Report)		
Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
19. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)		
Flare	Magnesium	Self-heating
Aluminum	Laminac	Trip flare
Sodium nitrate	Viton	Hydrogen
Exotherm	Gassing	Tungsten
Transition metal compounds		
Fuel		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)		
<p>A very broad investigation has been conducted on the utilization of powdered aluminum as a substitute fuel for atomized magnesium in pyrotechnic illuminant compositions developed primarily for the M49A1 trip flare.</p>		

DD FORM 1 JAN 73 1473

EDITION OF 1 NOV 68 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

DN

282 900

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

20. Abstract (Continued)

↓
Studies were conducted on the combustion and propagative characteristics of powdered aluminum/sodium nitrate mixtures. These studies included the effects of particle size, fuel-oxidant ratio, binder concentration, additives, fuel coating, flare case materials, flare case coatings and moisture.

Thermal analytical studies of aluminum/sodium nitrate systems provided conclusive evidence of a low temperature exotherm (70°C-135°C) which produces self-heating of the compositions in the presence of moisture.

A formulation utilizing powdered aluminum as a substitute fuel for atomized magnesium has been developed for use in the Army M49A1 trip flare. The burning characteristics of the composition containing 35% six micron powdered aluminum, 53% sodium nitrate, 7% seven micron tungsten powder and 5% Laminac 4116 polyester are adequate to meet the requirements of the M49A1 trip flare. By careful exclusion of moisture during processing, this composition demonstrated long term storage stability at elevated, ambient and low temperatures. ↙

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

The citation in this report of the names of commercial firms or commercially available products or services does not constitute official endorsement or approval of such commercial firms, products, or services by the US Government.

TABLE OF CONTENTS

	<u>Page No.</u>
Foreword	1
Introduction	3
Results and Discussion	4
Cassing and Self-heating of Al/NaNO ₃ compositions	8
Conclusions	11
Experimental Procedure	11
Blending	11
Loading	11
Testing	12
List of Materials Used	12
References	14
Distribution List	37
Tables	
1 Performance characteristics obtained March 1968 for Al/NaNO ₃ additive compositions	15
2 Effects of manganese carbonate and Laminac on performance characteristics of aluminum/sodium nitrate compositions	16
3 Performance characteristics of Al/NaNO ₃ compo- sitions in various coated flare cases	
a Paraffin coated Kraft paper cases	17
b Viton A coated Al trip flare cases	18

c	Laminac 4116 coated Al trip flare cases	19
d	Laminac/asbestos coated Al trip flare cases	20
4	Comparison of past and present performance characteristics of Al/NaNO ₃ /2% MnCO ₃ /5% Laminac compositions	21
5	Effect of case material and case liners on performance characteristics of aluminum/sodium nitrate/manganese carbonate/Laminac 4116 (35/58/2/5 composition)	22
6	Effect of various additives on performance characteristics of aluminum/sodium nitrate/Laminac 4116 in M49A1 trip flare case	23
7	Effect of aluminum content on performance characteristics of aluminum/sodium nitrate/Laminac 4116 with optimum additives in M49A1 trip flare case	24
8	Effect of ferric oxide on the performance characteristics of aluminum/sodium nitrate/Laminac 4116 composition (38/52/5) in M49A1 trip flare case	25
9	Performance characteristics of aluminum (Alcoa and Alcan)/sodium nitrate compositions	26
10	Effect of magnesium as an additive on performance characteristics of aluminum/sodium nitrate/tungsten/Laminac 4116 composition in M49A1 trip flare case	27
11	Sixteen-hour temperature conditioning test on performance characteristics of optimum aluminum fueled composition in assembled M49A1 trip flare	28
12	Four-month storage surveillance of performance characteristics of optimum aluminum fueled composition in assembled M49A1 trip flares	29

13	Amount of hydrogen generated by powdered aluminum	30
14	Effect of isostearic acid coated aluminum powder on performance characteristics in M49A1 trip flare case	31

Figures

1	DTA showing early appearance of low temperature exotherm in Al/NaNO ₃ composition after exposure to 52% RH atmosphere, ignition temperature - 915°C	32
2	DTA showing low temperature exotherm developed by Al/NaNO ₃ composition after exposure to 79% RH atmosphere	33
3	Development of 135°C exotherm in Al/NaNO ₃ compositions exposed to increasing amounts of moisture. All DTA's employed 2 g samples of 45/55 Al/NaNO ₃ at heating rate of 9.6°C/min, X-axis = 5.0 mv/in., Y-axis = 0.5 mv/in.	34
4	DTA showing the thermal behavior of a complex Al/NaNO ₃ system conditioned at 50% RH	35
5	DTA showing the appearance of a low temperature exotherm (\cong 125°C) in a complex Al/NaNO ₃ composition after conditioning at 90% RH	36

FOREWORD

Shidlovsky in his memorable treatise entitled *Fundamentals of Pyrotechnics* (Ref 1) appearing in the Russian book *Osnovy Piroteckhniki* (1964) states:

"The combustible substances used in pyrotechnic compositions must satisfy the following basic requirements:

1. They must have a heat of combustion providing for the best special effect of the composition;
2. They must oxidize adequately by means of the oxygen in the oxidizer or by means of the oxygen in the air.
3. They must give products in combustion that provide for obtaining the best special effect of the composition;
4. They must require the minimum quantity of oxygen for their combustion;
5. They must be chemically and physically stable in the temperature interval from -60 to +60°C, and be as stable as possible to the effect of weak solutions of acids and alkalis;
6. They must be nonhygroscopic;
7. They must be easily pulverized;
8. They must not have any toxic effect on the human organism;
9. They must be easily obtainable materials that are not in critically short supply."

If we examine the chemical and physical properties of the various metals available, we arrive at the fact, as also pointed out by Shidlovsky, that the following six substances constitute high energy combustibles: lithium, beryllium, magnesium, calcium, aluminum, titanium, and zirconium. If we apply Shidlovsky's criteria, lithium and calcium are

unusable pyrotechnic fuels because of their energetic reactivity to the moisture and oxygen of the air. Beryllium, as always, is avoided because of its extreme toxicity. Titanium and zirconium are used in igniter and delay applications rather than flares because of their high cost. Consequently we are left with magnesium and aluminum.

Classically, magnesium is superior to aluminum as a pyrotechnic fuel for two reasons. First, magnesium does not have a protective oxide coating but aluminum does. Second, magnesium has a higher vapor pressure than aluminum, as shown below, which allows it to vaporize rapidly and to be oxidized by the oxygen of the air. Aluminum vaporizes with difficulty and is generally spewed out of the flare as incandescent particles.

<u>Metal</u>	<u>Vapor Pressure</u>		
	<u>1 Torr</u>	<u>10 Torr</u>	<u>760 Torr</u>
Mg	621°C	743°C	1107°C
Al	1284°C	1487°C	2056°C

In the following report, the possible use of atomized aluminum powder-additive systems as a potential alternate fuel for magnesium is discussed. This study shows that a substitute aluminum based formulation has been developed which exceeds the minimum performance requirements of 35,000 candles for 55 seconds in the M49A1 trip flare. This composition contains 35% six micron atomized aluminum, 53% sodium nitrate, 7% seven micron tungsten powder and 5% Laminac 4116 polyester resin.

The two basic advantages of aluminum over magnesium are cost (38 cents per pound as compared to 85 cents for 20/50 mesh atomized magnesium) and ready commercial availability.

The disadvantages of the aluminum system, when exposed to moisture, are significant gassing, possible self-ignition. By careful exclusion of moisture during processing, this phenomenon can be eliminated, as was demonstrated by long-term storage stability testing.

INTRODUCTION

The present study was conducted to determine if a composition could be developed for the Army M49A1 trip flare containing aluminum as a substitute for magnesium. The primary justification for this program was based on cost and availability of aluminum as opposed to magnesium. Atomized magnesium powder is primarily produced for pyrotechnic applications, while powdered aluminum is mass-produced for a host of applications ranging from pigments in paints to energy constituents in propellants and explosives.

Although the study was directed primarily toward the trip flare, it delves into all aspects of flare technology. For example investigations were made of the effects of particle size, fuel-oxidant ratio, binder concentration, additives, fuel coating, flare case materials, flare case coatings, moisture, and short and long-term stability.

Previously, aluminum was not considered to be a good fuel for flare applications since mixtures of atomized aluminum (diameter $> 15\mu$) and sodium nitrate ignite poorly, propagate poorly, and burn very erratically and inefficiently. One of the reasons for the inefficiency of the Al/NaNO_3 system is that it produces a profusion of incandescent particles. This Roman Candle effect makes the flare an incendiary device as well as an illumination source. This incendiary aspect is very undesirable, possibly causing harm to users and starting ground fires.

A few years ago, however, it was demonstrated that powdered aluminum in combination with sodium nitrate (Ref 2,3) will burn propagatively when small quantities of various transition metals or metal compounds are incorporated into the mixture. These studies showed that the transition metal compounds affecting the Al/NaNO_3 reaction fell into five classes. Class 1 compounds are those which increase the efficiency of the system by decreasing the thermal conductivity of the basic binary. Class 2 compounds, consisting of manganese oxides, catalyze the normal decomposition of sodium nitrate to evolve oxygen at low temperatures. Compounds which cause ignition of aluminum at about 700°C (a value well below its normal ignition temperature of 1000°C) are in Class 3. Class 4 embraces transition metals which ignite with sodium nitrate at lower temperatures than aluminum. Finally, Class 5 compounds are those which alter the normal decomposition pattern of sodium nitrate, causing the evolution of the oxides of nitrogen at the melting point of the nitrate.

RESULTS AND DISCUSSION

As stated in the Introduction, previous studies showed that the combustion properties of Al/NaNO₃ compositions can be dramatically improved by the addition of certain additives (Ref 2,3). Since an inefficient Mg/NaNO₃/Laminac composition* is presently employed in the M49A1 trip flare (higher candlepower apparently not required), it was not difficult to meet the basic trip flare requirements of 35,000 candles and minimum burning time of 55 seconds.

The performance characteristics of the basic Al/NaNO₃/2% MnCO₃ (previously found to be the best additive system) and the total system Al/NaNO₃/2% MnCO₃/5% Laminac binder 4116 were gathered from Reference 2 and are presented in Table 1. To simplify the analysis of this data, a comparison of the absolute values of the various performance characteristics is presented in Table 2 together with percentage changes in the parameters with respect to the basic binary system. It is seen that the additive MnCO₃ produced marked reductions in burning rates and caused sizeable increases in light output and efficiencies. One interesting and unfortunate finding was that the addition of Laminac binder reduced the beneficial effects of the MnCO₃.

A series of Al/NaNO₃/2% MnCO₃/5% Laminac compositions were loaded into paper and aluminum trip flare cases. The cases were coated internally with a variety of case coatings. The purpose of these experiments was threefold. First, to see if the performance characteristics obtained were comparable to those previously obtained with flares made in 1968 (Ref 2). Second, to determine the effect of case material on performance characteristics. Finally, to determine if the Laminac/asbestos coating is the optimum insulator for use with the metal trip flare case. The performance characteristics obtained in these tests are presented in Tables 3a through 3d.

*A composition employing Mg/NaNO₃/Laminac in respective proportions of 65/25/10 will provide 154,000 candles for essentially 40 seconds duration and an efficiency of 46,000 candleseconds/gram.

As previously stated, the first goal was to determine how the characteristics of the present flares compared to those made six years ago. Table 4 makes this comparison and shows that the performance characteristics of the flare are quite comparable, especially in their luminous efficiencies.

The second goal of these experiments was to determine the effects of the two different flare cases. Table 5 shows the performance characteristics obtained using Kraft paper cases versus aluminum cases. The metal cases used are those employed to make M49A1 production items. These cases are extruded and have a wall thickness of 1/16 inch. The data in Table 5 shows two interesting facts. First, changing the case from paper to aluminum results in only a 15% reduction in the luminous output of the flares. In fact, the luminous output was only minimally affected using aluminum cases, regardless of case liner material. Second, and more important, nearly equivalent burning rates were realized in both paper and metal cases, provided that an excellent insulating liner such as Laminac/asbestos was employed. When either Viton A or Laminac was used, the total achievable time was reduced from ≈ 100 to ≈ 59 seconds. This demonstrates that without an insulator, heat is transferred down the metal tube causing preheating and rapid burning of the composition. Furthermore, the data of Table 5 presents an unusual case in flare behavior. Normally, an increase of nearly 50% in the burning rate of a flare, such as that occurring when changing from Kraft paper to Laminac coated aluminum, would have resulted in a significant increase in luminous output. In the present case, however, this did not occur. The luminous output remained approximately the same.

The next step in the program was to determine if MnCO_3 was the best additive for the Al/NaNO_3 system when using an aluminum case as it was for a paper case. Using the efficient 40/48 Al/NaNO_3 system as a base, a number of formulations was made and loaded containing the following additives (based on previous studies, Ref 2 and 3): 5% ferric oxide (red), 5% chromium sesquioxide, 7% tungsten powder, and 3% manganese carbonate. The performance characteristics obtained with these formulations are presented in Table 6. The data obtained shows that all of the compositions produced candlepower values in excess of 35,000 candles, the minimum requirement. During these tests, a significant observation was made. The flares containing ferric oxide and tungsten exhibited a marked reduction in the amount of incandescent

particles ejected. In view of this result, as well as the candlepowers produced, ferric oxide, tungsten and chromium sesquioxide were selected for further evaluation. New additive formulations were made using reduced percentages of aluminum powder in order to increase the burning time of the systems. The performance characteristics obtained for these new formulations are presented in Table 7 and show that several of the systems give outputs meeting the minimum requirements of the M49A1 flare. Based upon these results as well as visual evaluation, the compositions employing 7% tungsten powder (FY-1639) and 5% ferric oxide (FY-1634) were chosen as prime candidates for the M49A1 flare. Confirmation tests of these two systems showed that the tungsten system gave the same results but the ferric oxide one did not. It was discovered that the change in the performance characteristics of the ferric oxide system was due to the use of a new lot of material. From a purely cost advantage, it would be more desirable to use ferric oxide than tungsten. Consequently, some efforts were expended to characterize the old and new ferric oxides. An X-ray analysis of the original material showed the presence of 10% silicon dioxide (alpha quartz form), while the new material contained no silicon dioxide.

Table 8 presents the results of experiments to determine if other forms of ferric oxide or ferric oxide plus silicon dioxide (Superfloss, Johns-Manville Company) could be employed to produce desirable performance characteristics. It was found that the jeweler's rouge form of ferric oxide, as well as silicon dioxide (Superfloss), gave performance characteristics approaching that of the composition containing unknown grade ferric oxide. However, these systems were abandoned because both of them did not reduce the profuse production of incandescent aluminum particles. It was decided to continue the investigation using the tungsten formulation because of its superior performance characteristics.

A comparative investigation was next conducted using a lower cost atomized aluminum obtained from the Alcoa Corporation. This material costs \$0.38/lb per 450 pounds whereas the Alcan material previously employed was in excess of \$1.00/lb. The results of this comparison are presented in Table 9 and show that the lower cost Alcoa aluminum gave performance characteristics comparable to the more expensive 8 μ Alcan aluminum.

Before subjecting the tungsten additive system to the necessary storage and safety tests, a final attempt was made to further improve the luminous efficiency of the $\text{Al}/\text{NaNO}_3/\text{W}$ system by adding small percentages of 20/50 mesh atomized magnesium. As Table 10 shows, the addition of 5% or 10% atomized Mg did not produce any increase in the efficiency of the system while resulting in slightly increased burning rates. This data did not indicate any advantage in utilizing Mg in the $\text{Al}/\text{NaNO}_3/\text{W}$ system.

The finalized 35/53/7/5 $\text{Al}/\text{NaNO}_3/\text{W}/\text{Laminac}$ system was loaded into M49A1 flare cases and then incorporated into final end items. Two groups of these end items were subjected to two temperature extremes for 16 hours. One group was maintained at 75°C (hot), while the other was kept at -54°C (cold). After conditioning at these temperatures, the flares were examined visually and their performance characteristics determined. Table 11 shows that no deleterious results occurred due to conditioning at these extreme temperatures.

Standard sensitivity characteristics were determined for the $\text{Al}/\text{NaNO}_3/\text{W}/\text{Laminac}$ system. The values obtained are as follows.

Impact test, PA apparatus → 21 inches

Friction pendulum, steel shoe → no action

Electrostatic initiation, minimum joules → >11.025

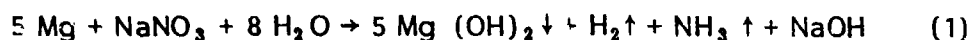
Ignition temperature, five second value → 564°C

The sensitivity values obtained indicate that only normal safeguards are required during blending and loading operations.

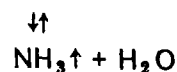
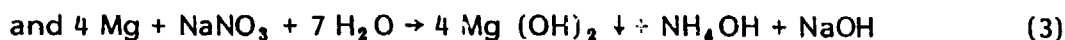
A series of M49A1 trip flares were loaded using FY-1639 composition (35% atomized Al, 53% NaNO_3 , 7% W, and 5% Laminac resin binder). This group of flares was placed in storage for four months at both ambient and 75°C. Table 12 shows the results obtained at monthly intervals over the four-month period. The data obtained clearly indicates that no degradation occurred in the performance characteristics of the Al composition during this extended storage period.

GASSING AND SELF-HEATING OF Al/NaNO₃ COMPOSITIONS

One of the basic properties of pyrotechnic compositions leading to instability in storage is their reactivity to moisture. The troublesome gassing occurring in Mg systems is attributable to the well known reaction:



This reaction is the summation of the following two fundamental ones:



The generation of NH₃ and H₂ gases by Equation 1, of course, is greatly accelerated with increasing temperature. Munition items in extended storage often suffer damage such as ruptured closure seals and split cases due to this unwanted generation of gases.

The gaseous as well as thermal output of reaction 1 is moderated by the insolubility of the magnesium oxide in the increasing alkalinity of the medium resulting from the products of NaOH. This growing insolubility follows from the rudimentary equilibrium process shown by the following equation.



As the concentration of the OH⁻ ion increases, the equilibrium shifts to the left favoring the formation of the protective coating or at least saturating the solution with Mg(OH)₂, thereby preventing dissolution of the metal coating.

Consider now the case of aluminum. The reaction of Al with moisture and sodium nitrate is shown in the following equation.



Unlike the Mg reaction, the aluminum oxide coating and $\text{Al}(\text{OH})_3$ formed are quite soluble in the resulting alkaline medium. Consequently, reaction 5 which produces NH_3 (probably also some H_2 by the reaction $2\text{Al} + 6\text{H}_2\text{O} \rightarrow 2\text{Al}(\text{OH})_3 + 3\text{H}_2 \uparrow$) and heat proceeds at an accelerating rate. This latter process eventually causes extensive self-heating and, under certain conditions, spontaneous ignition of the composition.

The Al composition developed in this program, FY-1639, exposed to an uncontrolled ambient environment for a few days, generated (11+) ml of gas in five minutes duration at 120°C temperature using the standard vacuum stability test. When another sample of this composition was dried at 105°C for 16 hours prior to conducting the vacuum stability test, only 0.35 ml of gas was produced after 40 hours at 120°C . This result demonstrates that a stable Al composition can be processed and loaded by rigorous exclusion of moisture.

Table 13 summarizes data obtained from the Alcoa Corporation which shows the amount of gas produced by refluxing powdered aluminum in a 20% ammonium nitrate solution. This data shows the effect of changing the particle size on gassing and how this gassing can be significantly reduced by coating the metal with isostearic acid. When isostearic acid coated aluminum was employed in the FY-1639 formulation, however, it was found, as shown in Table 14, that a marked reduction occurred in both candlepower and efficiency. For example, the candlepower was reduced from 50,000 to 31,000 candles and the efficiency went from 17,000 to 12,000 candleseconds/gram. Consequently, the more feasible method to eliminate gassing is rigorous drying rather than coating the metal.

Although the gassing of the aluminum/sodium nitrate composition is an annoying problem, the more serious danger is that of self-heating leading to spontaneous ignition. A good discussion of this phenomenon is given by Johansson and Persson in the Swedish journal *Pyroteknikdoggen* (Ref 4).

Figure 1 shows the DTA of a simple 45/55 Al^F (6 μ)/ NaNO_3 composition which had been conditioned at 52% RH for six days. As is seen, the pattern is quite complex having three primary exotherms at approximately 135°C , 690°C , and 915°C . The last exotherm resulted in ignition. When the same Al/ NaNO_3 composition was conditioned at a higher RH of 79% for the same

length of time, six days, a different DTA pattern resulted as shown in Figure 2. Here the small exotherm at 135°C grew tremendously in intensity, and ignition occurred at the second exotherm at 690°C. With increased mass and confinement, ignition occurs easily in the region of the first exotherm, at temperatures as low as 60°C to 70°C.

Figure 3 shows that the exotherm at 135°C is solely dependent upon moisture content. In the DTA (a), no exotherm appears for a perfectly dry Al/NaNO₃ sample. Some activity begins to appear in run (b) when the same Al/NaNO₃ composition is exposed to a 79% RH atmosphere for 22 hours. Finally, the DTA in (c) clearly shows the dramatic growth of the exotherm using a sample which had been exposed to a 79% RH atmosphere for 66 hours.

In another program design to furnish a highly exothermic composition for rocket assisted projectiles, an Al composition was developed containing the additive MnCO₃. This highly metalized composition contained 85/10/2/5 Al (6μ)/NaNO₃/MnCO₃/Viton A. Figure 4 presents the DTA behavior for the basic composition which had been conditioned at 50% RH for five weeks. This composition exhibited no low temperature exotherm and ignited immediately following the melting of NaNO₃ at approximately 300°C. This ignition behavior is peculiar to aluminum/NaNO₃ systems containing additives such as inorganic fluorides (e.g., NaF) and organic fluorides (e.g. Viton). It has been hypothesized by many that at the melting point of NaNO₃, the additive either removes and/or makes the aluminum oxide protective coating permeable so that an immediate reaction occurs between the clean Al surface and the molten oxidant.

When this additive composition was exposed to a 90% RH atmosphere for five weeks, the same low temperature exotherm occurred as with the Al/NaNO₃ binary. This phenomenon is clearly seen in Figure 5. Consequently, it appears that the presence of moisture sensitizes simple as well as complex Al/NaNO₃ systems. Studies are presently being conducted to determine the nature of the intermediate which causes the low temperature ignition of Al/NaNO₃ systems. This intermediate is probably NaOH which reacts exothermally with both Al and its protective coating.

CONCLUSIONS

A formulation has been developed for use in the U.S. Army Trip Flare which utilizes aluminum instead of magnesium for a fuel. This composition contains 35% six micron atomized aluminum, 53% sodium nitrate, 7% seven micron tungsten powder and 5% Laminac 4116 polyester resin.

Two basic advantages of the new aluminum system are cost (38 cents per pound for aluminum as compared to 85 cents a pound for 20/50 mesh atomized magnesium) and ready commercial availability.

The disadvantages of the aluminum system are gassing and self-heating which occur when it is exposed to excess moisture. By careful exclusion of moisture during processing, however, these effects can be eliminated as was demonstrated by long-term storage stability testing.

EXPERIMENTAL PROCEDURE

Blending

The compositions cited in this report were blended in a Lancaster counter-current mixer, model PC, which imparts a mulling-type action to the constituents of the blend. The sodium nitrate was dried for 24 hours at 110°C prior to use. The resultant flare compositions were dried in trays containing a one-inch thickness of composition for a minimum of 16 hours at 105°C.

Loading

Each composition was loaded in four equal increments at a pressure of 10,000 psi. Ten grams of DP-1886 igniter composition (65% five micron tungsten powder, 24% barium chromate, 10% potassium perchlorate and 1% Vinyl Alcohol Acetate Resin MA-28-18) were used as the first fire. Ten grams of Laminac coated fireclay were used as an inert charge at the bottom of the Kraft paper cased flares. The interior walls of the flare cases were coated with the materials indicated in the tables.

Testing

Light measurements of the flares were determined in accordance with MIL-P-20464 except that a black background was used instead of a white one.

LIST OF MATERIALS USED

Aluminum powder, atomized, Lot No. 1072, average particle diameter 6.2 microns, Aluminum Company of Canada

Aluminum powder, atomized, Lot No. 1401, average particle diameter 8.0 microns, Aluminum Company of America

Sodium nitrate, double refined, USP grade, average particle diameter 35 microns, Davies Nitrate Company

Tungsten powder, Lot No. 6154D, average particle diameter 6.7 microns, General Electric Company

Magnesium powder, atomized, 20/50 mesh, Specification MIL-P-14067B, Hart Metals Incorporated

Ferric oxide, red, unknown grade, lot, company

Ferric oxide, jeweler's rouge, catalogue No. 1-115, average particle diameter 0.6 microns, Fisher Scientific Company

Ferric oxide, reagent grade, catalogue No. 1-116, average particle diameter 0.5 microns, Fisher Scientific Company

Chromium sesquioxide, Lot 32194, average particle diameter 2 microns, J.T. Baker Chemical Company

Sodium fluoride, S-299, average particle diameter 8.6 microns, Fisher Scientific Company

•
Superfloss (SiO_2), Johns-Manville Company

• Cab-O-Sil (SiO_2), MS-7, Cabot Corporation

Magnesium, atomized, 30/50 mesh, Specification MIL-P-14067B, Hart
Metals Incorporated

Laminac polyester resin 4116, American Cyanamid Company

Vinyl alcohol acetate resin, MA-28-18, Palmer Cement Company

Viton A fluorocarbon resin, Dupont Chemical Company

Asbestos powder, technical grade, Lot No. 51971, Fisher Scientific
Company

REFERENCES

1. Shidlovsky, A., *Fundamentals of Pyrotechnics, (Osnovy Piroteckhniki)*, Picatinny Arsenal Technical Memorandum 1615, May 1965
2. Jackson, B., Kaye, S.M., and Taylor, F.R., *Aluminum Powder as an Alternate Fuel for Magnesium in Illuminant Compositions*, Picatinny Arsenal Technical Report 3713, November 1968
3. Leader, P.J., Westerdahl, R.R., and Taylor, F.R., *The Effects of Some Transition Metal Compounds on the Performance Characteristics of Aluminum/Sodium Nitrate Compositions*, Picatinny Arsenal Technical Report 3846, May 1969
4. Johansson, S.R. and Persson, K.G., *Explosion Hazards of Pyrotechnic Aluminum Compositions*, *Pyroteknikdogen*, Stockholm, 10 May 1971, pp 74-90

Table 1
Performance characteristics obtained March 1968 for
Al/NaNO₃/additive compositions

	Percent ingredients								
	35	45	55	35	45	55	35	45	55
Aluminum powder, atomized, 6.2 microns	35	45	55	35	45	55	35	45	55
Sodium nitrate, USP, 35 microns	65	55	45	63	53	43	58	48	38
Manganese carbonate, 2 microns				2	2	2	2	2	2
Laminac resin 4116							5	5	5
<u>Performance characteristics</u>									
Burning rate, inches/min	4.7	7.6	8.8	2.6	6.6	10.1	2.0	3.4	4.4
Luminous output, kilocandles	30.7	76.5	37.4	50.2	120.8	120.7	18.6	46.6	43.9
Efficiency, kilocandlesec/g	9.7	14.5	6.2	26.5	26.2	16.9	13.2	18.9	13.2

Table 2

Effects of manganese carbonate and laminac
on performance characteristics of
aluminum/sodium nitrate compositions

Compositions	Burning rate		Light output		Efficiency	
	in./min	%Δ	Kilocandles	%Δ	kilocdle-sec g	%Δ
35/65 Al/NaNO ₃ +2% MnCO ₃ +2% MnCO ₃ +5% Lam	4.7		30.7		9.7	
	2.6	-44.7	50.2	+63.5	26.5	+173
	2.0	-57.4	18.6	-39.4	13.2	+ 36
45/55 Al/NaNO ₃ +2% MnCO ₃ +2% MnCO ₃ +5% Lam	7.6		76.5		14.5	
	6.6	-13.1	120.8	+57.9	26.2	+ 80.7
	3.4	-42.1	46.6	-39.1	18.9	+ 30.3
55/45 Al/NaNO ₃ +2% MnCO ₃ +2% MnCO ₃ +5% Lam	8.8		37.4		6.2	
	10.1	+14.8	120.7	+222.7	16.9	+172.6
	4.4	-50.0	43.9	+17.4	13.2	+112.9

Table 3a

Performance characteristics of Al/NaNO₃
compositions in various coated flare cases

Paraffin coated Kraft paper cases

Percent ingredients

Aluminum powder, atomized, 6.2 microns	35	45	55
Sodium nitrate, USP, 35 microns	58	48	38
Manganese carbonate, 2 microns	2	2	2
Laminac resin 4116	5	5	5

Performance characteristics

Burning rate, inches/minute	2.5	3.9	6.2
Burning time, seconds	100.3	63.2	31.4
Luminous output, kilocandles	24.7	49.4	52.1
Efficiency, kilocandlesec/g	15.1	19.0	12.5

Table 3b

Performance characteristics of Al/NaNO₃
compositions in various coated flare cases

Viton A coated Al trip flare cases

	<u>Percent ingredients</u>	
Aluminum powder, atomized, 6.2 microns	35	45
Sodium nitrate, USP, 35 microns	58	48
Manganese carbonate, 2 microns	2	2
Laminac resin 4116	5	5
<u>Performance characteristics</u>		
Burning rate, inches/minute	3.5	5.4
Burning time, seconds	59.5	37.9
Luminous output, kilocandles	21.4	61.2
Efficiency, kilocandlesec/g	7.8	14.2
		11.1
		7.5
		27.1
		67.1

Table 3c

Performance characteristics of Al/ NaNO_3
compositions in various coated flare cases

Laminac 4116 coated Al trip flare cases

	<u>Percent ingredients</u>		
Aluminum powder, atomized, 6.2 microns	35	45	55
Sodium nitrate, USP, 35 microns	58	48	38
Manganese carbonate, 2 microns	2	2	2
Laminac resin 4116	5	5	5
<u>Performance characteristics</u>			
Burning rate, inches/minute	3.7	6.6	9.3
Burning time, seconds	56.2	30.7	21.9
Luminous output, kilocandles	23.1	69.8	70.4
Efficiency, kilocandlesec/g	7.9	13.1	9.4

Table 3d

Performance characteristics of Al/NaNO₃
Compositions in various coated flare cases

Laminac/asbestos coated Al trip flare cases

Percent ingredients

Aluminum powder, atomized 6.2 microns
Sodium nitrate, USP, 35 microns
Manganese carbonate, 2 microns
Laminac resin 4116

35 45 55
58 48 38
2 2 2
5 5 5

Performance characteristics

Burning rate, inches/minute
Burning time, seconds
Luminous output, kilocandles
Efficiency, kilocandlesec/g

2.2 4.0 5.3
96.8 50.7 38.6
20.9 47.3 46.1
12.3 14.6 10.9

Table 4

Comparison of past and present performance characteristics
of Al/NaNO₃/2% MnCO₃/5% Laminac compositions

Percent Al	³⁵ (a)		45		55	
	Old	New	Old	New	Old	New
Burning rate, in./min	2.0	2.5	3.4	3.9	4.4	6.2
Luminous output, kilocandles	18.6	24.7	46.6	49.4	43.9	52.1
Efficiency, kilocandlesec/g	13.2	15.1	18.9	19.0	13.2	12.5

(a) Data obtained from flares made and tested in November 1968, all compositions loaded into 1.31 inch diameter Kraft paper cases lined with Paraffin

Table 5

Effect of case material and case liners on
performance characteristics of aluminum/sodium nitrate/manganese
carbonate/Laminac 4116 (35/58/2/5) composition

Case material: <u>Case liner:</u>	<u>Kraft paper</u>		<u>M49A1 trip flare case</u>	
	<u>Paraffin wax</u>	<u>Viton A</u>	<u>Laminac</u>	<u>Laminac/asbestos</u>
Burning rate, inches/minute	2.5	3.5	3.7	2.2
Total burning time, seconds	100.3	59.5	56.2	96.8
Luminous output, kilocandles	24.7	21.4	23.1	20.9
Efficiency, kilocandlesec/g	15.1	7.8	7.9	12.3

Table 6

Effect of various additives on performance characteristics
of aluminum/sodium nitrate/Laminac 4116
in M49A1 trip flare case

	Percent ingredients			
	42	42	40	42
Aluminum, atomized, 6.2 microns	48	48	48	50
Sodium nitrate, 35 microns	5	-	-	-
Ferric oxide (red)	-	5	-	-
Chromium sesquioxide	-	-	7	-
Tungsten, 4.5 microns	-	-	-	3
Manganese carbonate, 2 microns	5	5	5	5
Laminac resin 4116				
Performance characteristics	4.7	4.0	4.3	3.4
Burning rate, inches/ min	61.4	49.8	59.4	36.2
Luminous output, kilocandles	15.3	15.1	15.1	13.3
Efficiency, kilocandlesec/g	43.9	51.4	47.8	60.9
Burning time, seconds				

Table 7

Effect of aluminum content on performance characteristics of
aluminum/sodium nitrate/Laminac 4116 with optimum additives
in M49A1 trip flare case

	Percent ingredients						
Aluminum, atomized, 6.2 microns	36	38	40	30	35	38	39
Sodium nitrate, 35 microns	54	52	52	58	53	50	51
Ferric oxide (red)	5	5	3	-	-	-	-
Tungsten, 4.5 microns	-	-	-	7	7	7	-
Chromium sesquioxide, 2 microns	-	-	-	-	-	-	5
Laminac resin 4116	5	5	5	5	5	5	5
<u>Performance characteristics</u>							
Burning rate, inches/min	3.3	3.4	3.7	3.2	3.5	3.9	3.3
Luminous output, kilocandles	42.9	43.9	48.1	29.1	46.7	53.6	44.0
Efficiency, kilocandlesec/g	15.0	14.9	14.9	10.8	14.1	14.8	15.3
Burning time, seconds	61.3	59.7	54.9	71.0	61.1	53.0	61.1

Table 8

Effect of ferric oxide on the performance characteristics of
aluminum/sodium nitrate/Laminac 4116 composition
(38/52/5) in M49A1 trip flare case

Additives	Percent			
Ferric oxide, red, grade unknown	5	-	-	-
Ferric oxide, jeweler's rouge, 0.6 micron	-	5	-	-
Ferric oxide, reagent, 0.5 microns	-	-	5	4.5
Superfloss	-	-	5	0.5
<u>Performance characteristics</u>				
Burning rate, inches/min	3.7	3.3	3.1	3.5
Luminous output, kilocandles	46.5	40.3	35.3	44.7
Efficiency, kilocandlesec/g	15.9	15.3	14.6	16.0
Burning time, seconds	60.4	67.1	72.6	63.0
				74.3
				3.0
				34.6
				14.6
				74.3

Table 9

Performance characteristics of aluminum
(Alcoa and Alcan)/sodium nitrate compositions

Ingredients	FY Composition No.	
	1639	1571
Aluminum, atomized, 6.2 microns, Alcan, %	35	-
Aluminum, atomized, 8.0 microns, Alcoa, %	-	35
Sodium nitrate, USP, 35 microns, %	53	53
Tungsten powder, 6.7 microns, %	7	7
Laminac resin 4116, %	5	5
<u>Performance characteristics</u>		
Candlepower, kilocandles	49.9	47.5
Burning time, seconds	65.3	71.6
Luminous efficiency, kilocandlesec/g	16.9	17.7

Table 10

Effect of Magnesium as an additive on performance characteristics
of aluminum/sodium nitrate/tungsten/Laminac 4116 composition
in M49A1 trip flare case

Aluminum, atomized, 6.2 microns	35	35	35
Magnesium, atomized, 30/50 mesh	-	5	10
Sodium nitrate	53	48	50
Tungsten, 6.7 microns	7	7	-
Laminac resin 4116	5	5	5
<u>Performance characteristics</u>			
Burning rate, inches/min	3.6	4.2	4.0
Luminous output, kilocandles	50.2	54.2	54.0
Efficiency, kilocandlesec/g	15.6	15.0	15.9
Burning time, seconds	59.1	50.0	54.2

Table 11

Sixteen-hour temperature conditioning test on performance
characteristics of optimum aluminum fueled composition
in assembled M49A1 trip flare

Aluminum, atomized, 6.2 microns, %	35		
Sodium nitrate, 35 microns, %	53		
Tungsten, 6.7 microns, %	7		
Laminac resin 4116, %	5		
<u>Storage conditions</u>	<u>Ambient</u>	<u>75°C</u>	<u>-54°C</u>
<u>Performance characteristics</u>			
Burning rate, inches/min	3.3	3.5	3.6
Luminous output, kilocandles	43.6	47.2	44.6
Efficiency, kilocandlesec/g	14.1	13.8	13.7
Burning time, seconds	62.2	56.1	59.1

Table 12

Four-month storage surveillance of performance characteristics
of optimum aluminum fueled composition in assembled M49A1
trip flares

Storage period, months	Burning rate, inches/min		Luminous output, kilocandles		Efficiency kilocandlesec/g		Burning time, seconds	
	ambient	75°C	ambient	75°C	ambient	75°C	ambient	75°C
0	3.5	-	38.8	-	13.3	-	63.3	-
0.5	3.2	3.3	39.8	38.3	14.6	13.6	68.9	66.9
1	3.4	3.3	43.6	41.5	15.2	14.9	65.5	67.3
2	3.5	3.1	46.2	41.4	15.8	15.7	64.3	71.3
3	3.4	3.4	38.9	40.5	13.9	13.9	64.9	64.8
4	3.4	3.4	39.8	39.2	13.7	13.5	64.9	65.1

Table 13
Amount of hydrogen generated by powdered aluminum (a)

(Data provided by Research Labs, Alcoa,
New Kensington, PA)

Al particle diameter microns	MI gas produced	
	Untreated	Coated with (b) Isostearic acid
25-30	8	negligible
15	10	0-0.2
8	50-60	0-0.2

(a) Volume of gas produced by refluxing one gram at 93°C for six hours in a
20% ammonium nitrate solution

(b) Value depends on efficacy of coating

Table 14

Effect of isostearic acid coated aluminum powder on
performance characteristics in M49A1 trip flare case

	<u>Percent ingredients</u>	
Aluminum, atomized, 6.2 microns	35	-
Aluminum, atomized, coated with 4% isostearic acid, 8.5 microns	-	35
Aluminum, atomized, 8 microns	58	58
Sodium nitrate, 35 microns	7	7
Tungsten, 6.7 microns	5	5
Laminac resin 4116		
<u>Performance characteristics</u>		
Burning rate, inches/min	3.4	3.1
Luminous output, kilocandles	49.9	31.3
Efficiency, kilocandlesec/g	16.9	11.7
Burning time, seconds	65.3	72.3
		71.6

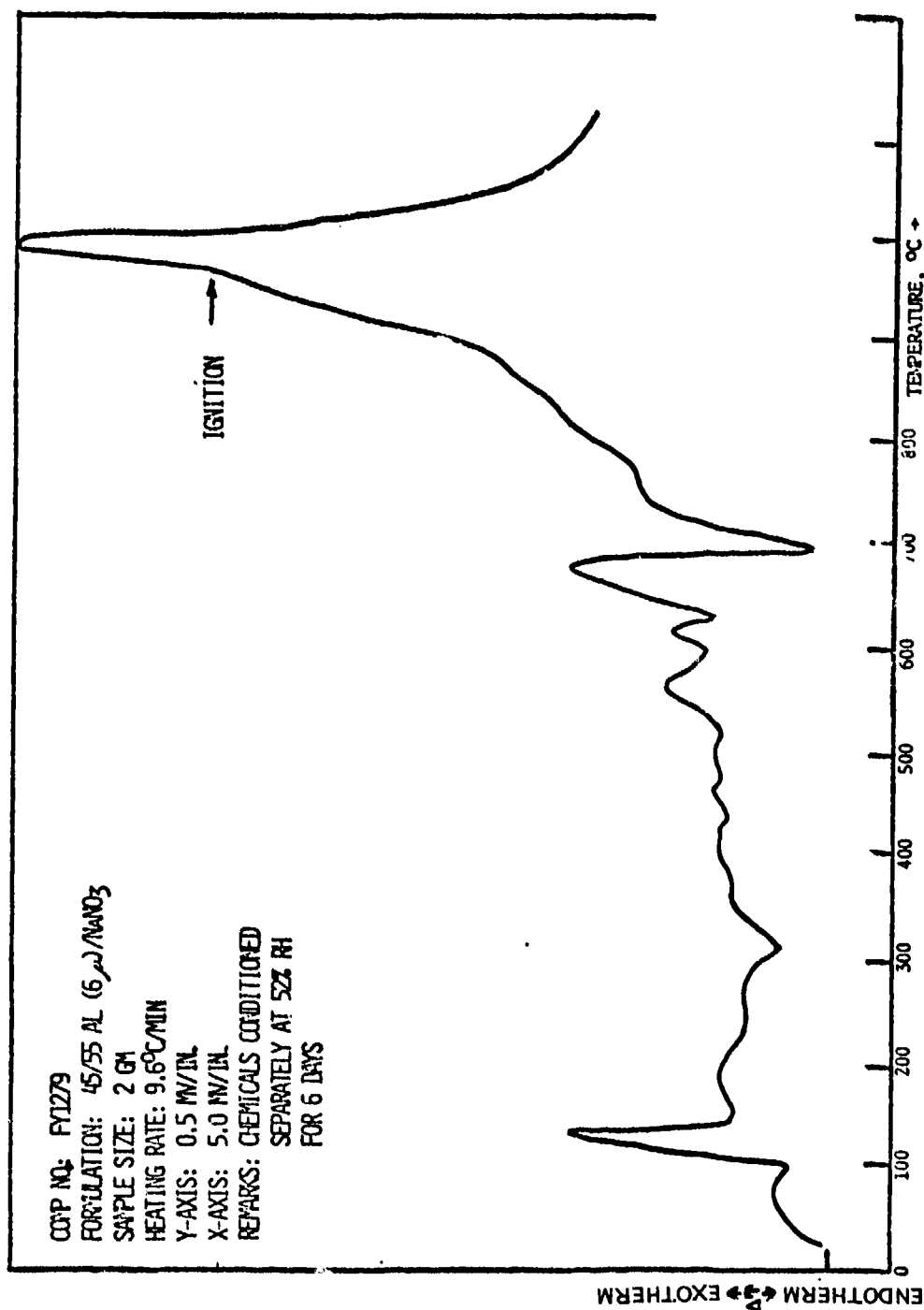


Fig 1 DTA showing early appearance of low temperature exotherm in Al/NaNO₃ composition after exposure to 52% RH atmosphere, ignition temperature = 915°C

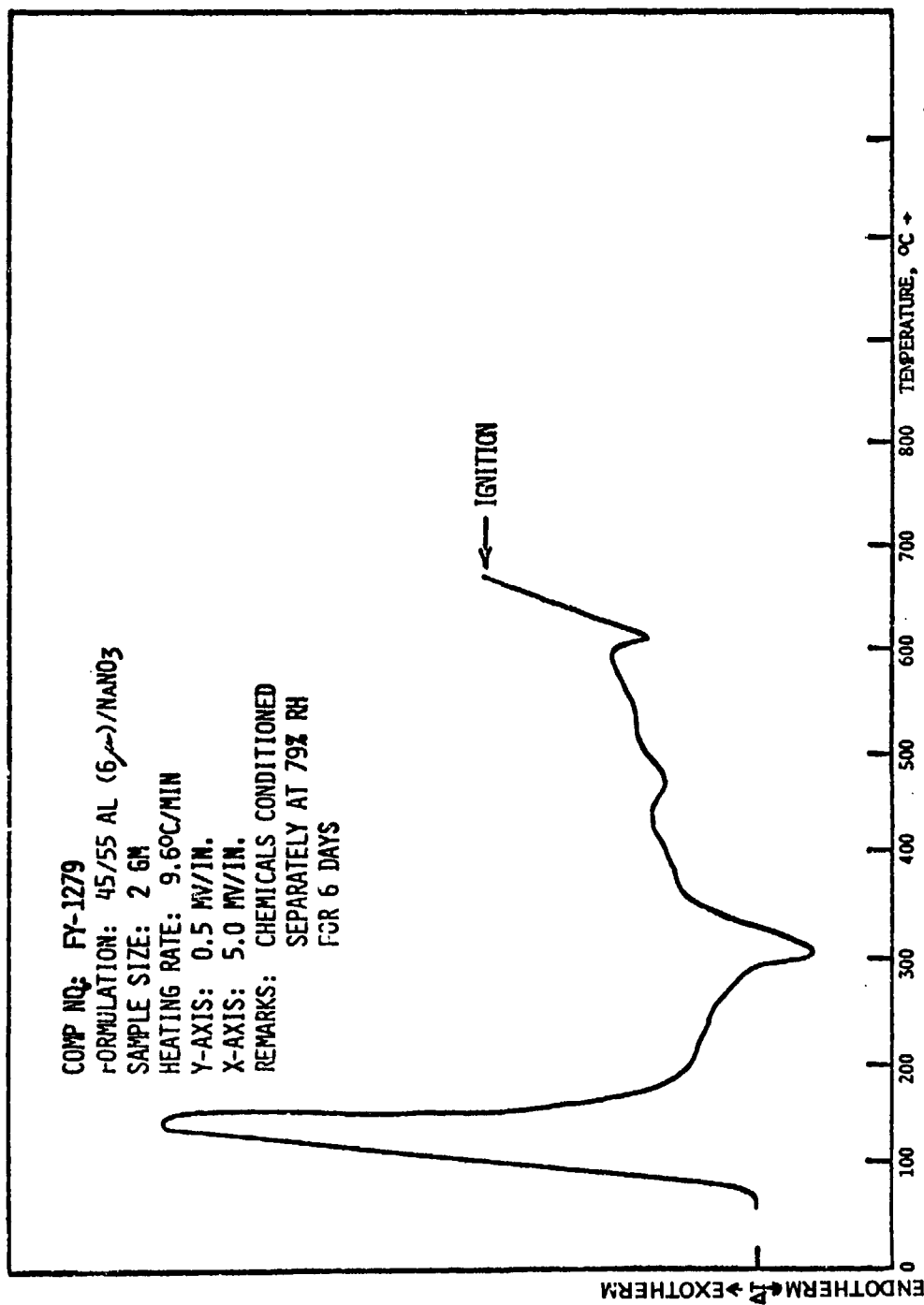


Fig 2 DTA showing low temperature exotherm developed by Al/NaNO₃ composition after exposure to 79% RH atmosphere

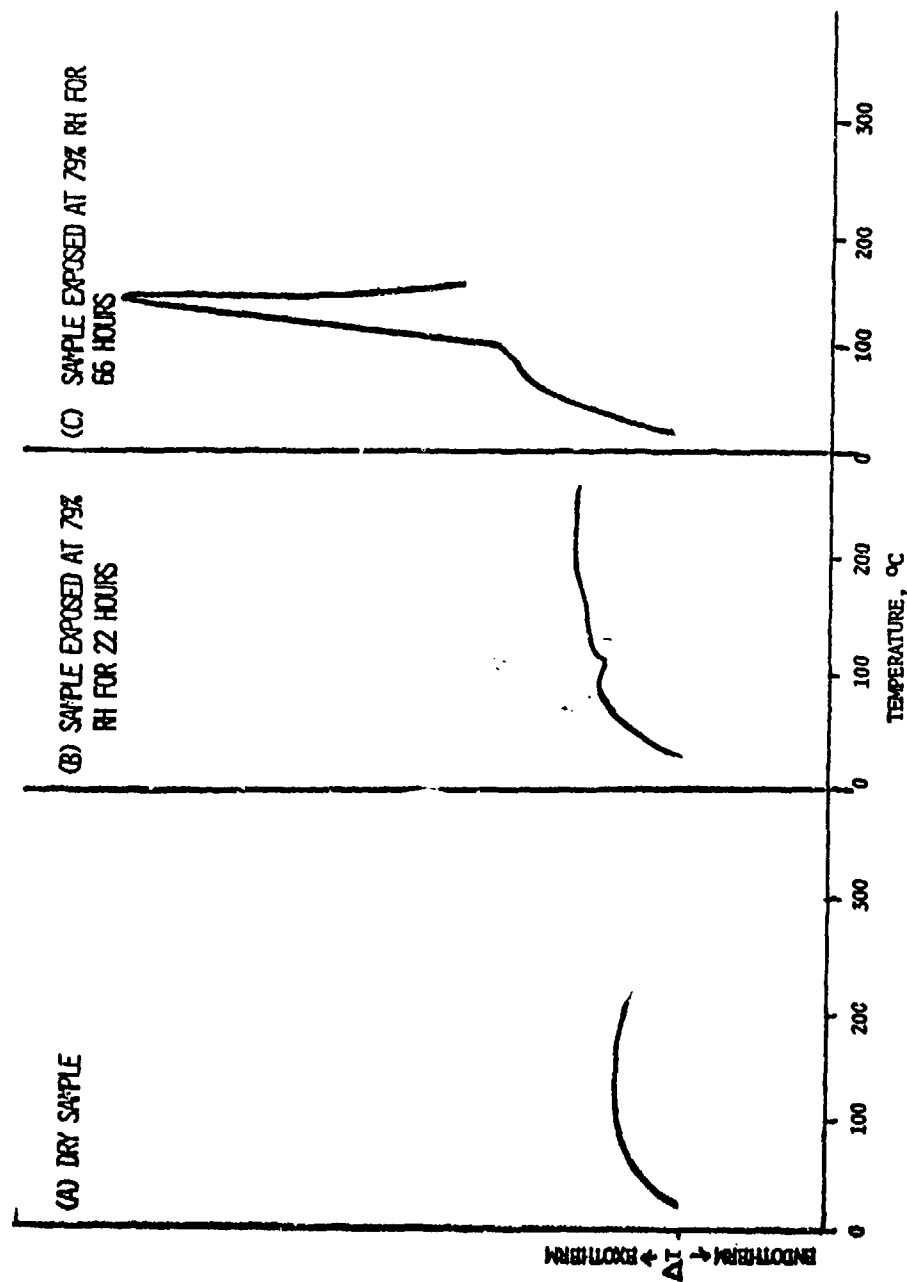


Fig 3 Development of 135°C exotherm in Al/NaNO₃ compositions exposed to increasing amounts of moisture, all DTA's employed 2 g samples of 45/55 Al/NaNO₃ at heating rate of 9.6°C/min, X-axis = 5.0 mv/in., Y-axis = 0.5 mv/in.

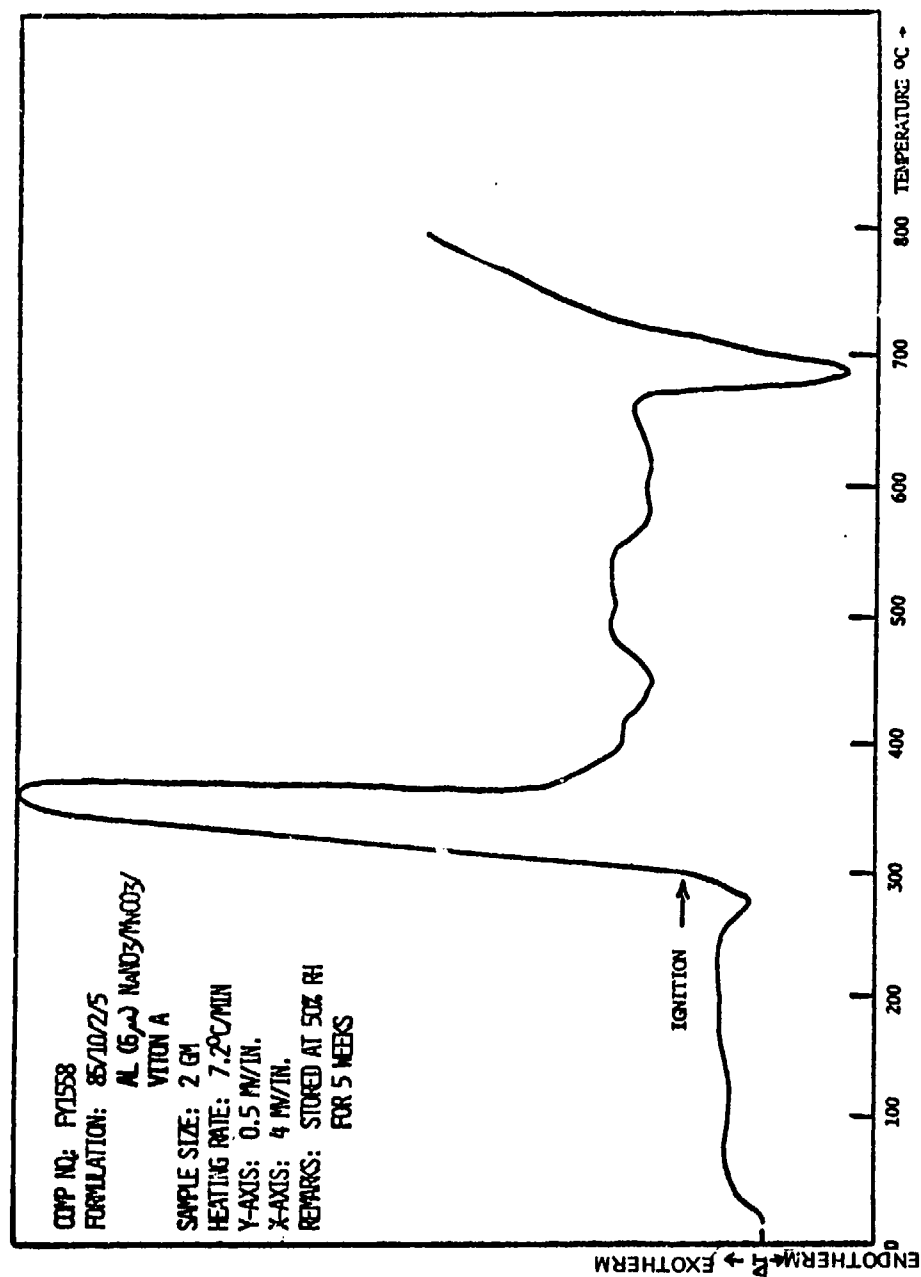


Fig 4 DTA showing the thermal behavior of a complex Al/NaNO₃ system conditioned at 50% RH

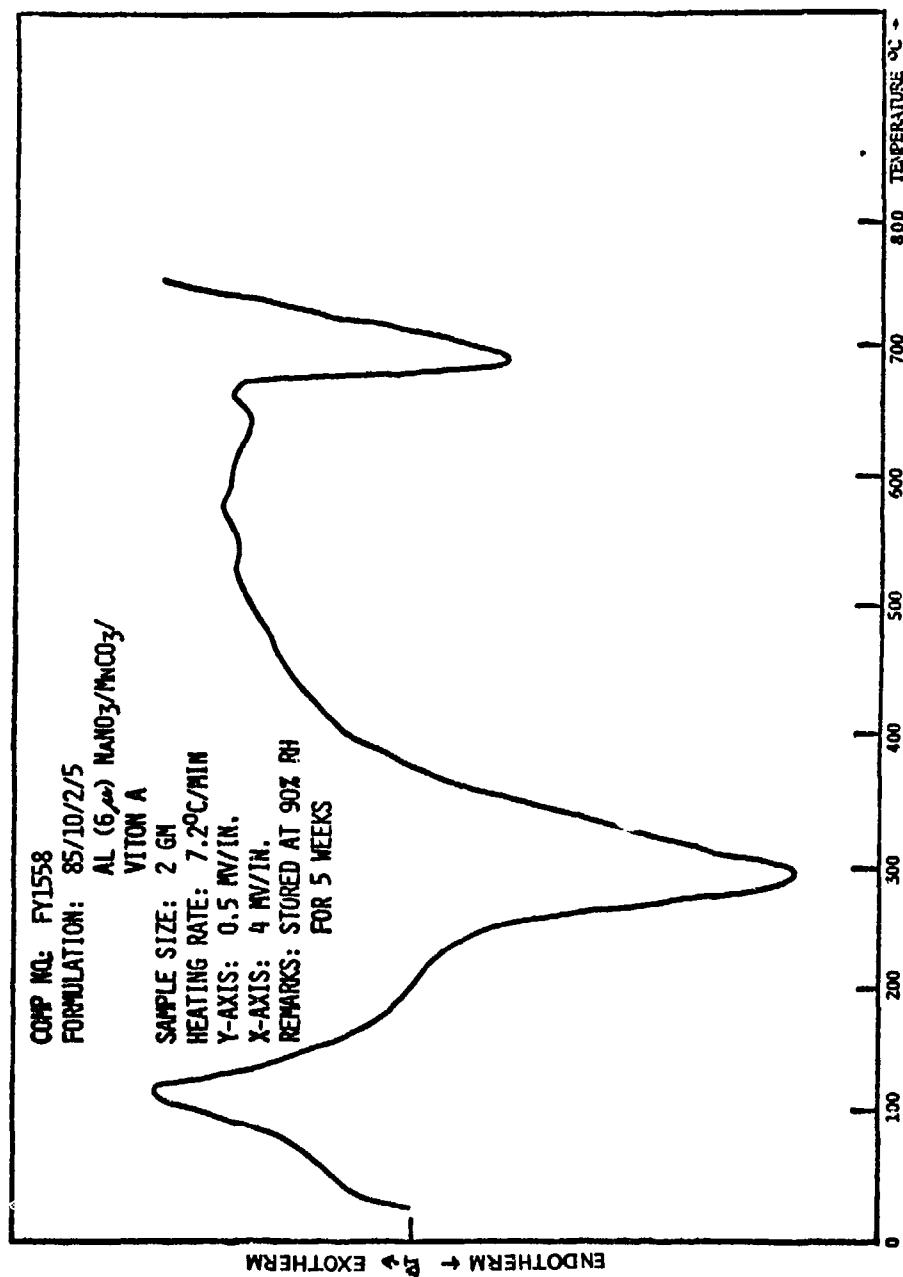


Fig 5 DTA showing the appearance of a low temperature exotherm ($\approx 125^\circ\text{C}$) in a complex Al/NaNO_3 composition after conditioning at 90% RH

DISTRIBUTION LIST

Copy No.

Commander	
Picatinny Arsenal	
ATTN: SARPA-TS-S	1-5
Mr. S. Fleischnick, ADED	6-9
Mr. H. D. Rutkovsky, ADED	10-12
Mr. D. Katz, ADED	13-15
Mr. E. Belitsky, ADED	16-18
Mr. J. Matura, ADED	19-21
Dover, New Jersey 07801	
Commander	
U.S. Army Materiel Command	
ATTN: Scientific and Technical Info Div	22
AMCRD-Q	23
AMCRD-RS	24
5001 Eisenhower Ave	
Alexandria, Virginia 22304	
Commander	
U.S. Army Armament Command	
ATTN: Scientific and Technical Info Div	25
AMSMU-RE	26
Rock Island, Illinois 61201	
Commander	
Aberdeen Proving Ground	
ATTN: STEAP-TL (Bldg 305)	27
Aberdeen Proving Ground, Maryland 21005	
Director	
U.S. Army Ballistic Research Laboratories	
ATTN: Scientific and Technical Info Div	28
Dr. J. Richard Ward	29
Aberdeen Proving Ground, Maryland 21005	

Commander Harry Diamond Laboratories ATTN: Library, Room 211, Bldg 92 Connecticut Ave and VanNess St, NW Washington, D.C. 20438	30
Commander U.S. Army Mobility Equipment R&D Center ATTN: Scientific and Technical Info Div Fort Belvoir, Virginia 22060	31
U.S. Army Foreign Science and Technology Center ATTN: AMXST-ISI 220 Seventh St, NE Charlottesville, Virginia 22901	32
Institute for Defense Analyses ATTN: Library, Documents 400 Army-Navy Drive Arlington, Virginia 22202	33
U.S. Army Research Office Box CM, Duke Station Information Processing Office Durham, North Carolina 27706	34
Defense Documentation Center Cameron Station Alexandria, Virginia 22314	35-46
Central Intelligence Agency ATTN: CRS/ADD/Standard Distribution Washington, D.C. 20505	47
Commander Frankford Arsenal ATTN: Scientific and Technical Info Div Pitman-Dunn Laboratory Philadelphia, Pennsylvania 19137	48 49

Commander	
U.S. Naval Ammunition Depot	
ATTN: Scientific and Technical Info Div	50
Chemical Sciences Division	51
Crane, Indiana 47522	
Commander	
Naval Weapons Center (Code 533)	
ATTN: Scientific and Technical Info Div	52
China Lake, California 93555	
Naval Ordnance Systems Command	
Department of the Navy	
ATTN: Code ORD-0632	53
Washington, D.C. 20360	
Commander	
U.S. Naval Ordnance Laboratory	
ATTN: Scientific and Technical Info Div	54
Silver Spring, Maryland 20910	
Commander	
U.S. Naval Ordnance Station	
ATTN: Scientific and Technical Info Div	55
Indian Head, Maryland 20640	
Commander	
Naval Air Systems Command	
Dept of the Navy	
ATTN: Code AIR-53221	56
Washington, D.C. 20360	
Commander	
U.S. Air Force	
ATTN: Scientific and Technical Info Div	57
AFATL/DLIP	58
Eglin Air Force Base, Florida 32541	

USAF/DCS Research and Development Pentagon Washington, D.C. 20330	59
Foreign Technology Division (DPXA) Wright-Patterson AFB, Ohio 45433	60
Commander Lowry Technical Training Center (TTOX) Lowry AFB, Colorado 80230	61
NASA Scientific and Technical Info Div P.O. Box 33 College Park, Maryland 20740	62
Denver Research Institute University of Denver ATTN: Mr. Robert Blunt Denver Colorado 80210	63
Battelle Memorial Institute Columbus Laboratories TACTEC 505 King Ave Columbus, Ohio 43201	64